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ADP012639

TITLE: Local Vibrational Modes of Carbon-Hydrogen Complexes in Proton Irradiated AlGaN

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ADP012585 thru ADP012685

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LOCAL VIBRATIONAL MODES OF CARBON-HYDROGEN COMPLEXES IN PROTON IRRADIATED AlGaN

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ABSTRACT

Local vibrational modes (LVMs) of carbon-hydrogen (C-H) complexes in proton implanted AlGaN grown on sapphire by metalorganic chemical vapor deposition (MOCVD) were investigated using Fourier transform infrared (FTIR) spectroscopy. The LVMs exhibit five distinctive peaks in the spectral region of $2846\text{--}2963\text{ cm}^{-1}$, which are due to the symmetric and asymmetric stretching modes of C-H_n ($n=1\text{--}3$). The LVMs intensities in doped AlGaN are increased as irradiation dose is increased in the entire irradiation dose range used without reaching the saturation stage. On the other hand, undoped samples show that LVMs intensity increase then either decreased or saturated as the irradiation dose is increased above $5\times 10^{16}\text{ cm}^{-2}$. Proton irradiation causes a drastic increase in the CH_3 LVM while electron irradiation causes the opposite effect suggesting strongly that the observed LVMs are truly due to CH complexes.

INTRODUCTION

Optoelectronic devices based on III-nitrides and their ternary alloys have a broad range of application due to their wide direct band-gaps covering the spectral range from visible to ultraviolet. GaN has unique applications in blue, green and ultraviolet-blue light-emitting diodes, detectors and laser diodes [1-4]. III-nitride material system also shows tremendous potential in the field of high-temperature and high-power electronics because of their superior materials parameters [5]. Omnipresent impurities such as C, H and O play detrimental and beneficial roles in fabrication processes. For example, hydrogen can passivate the acceptor Mg [6-8] in GaN. Hydrogen can be easily incorporated into III-nitride during or after the growth of the materials [8]. Therefore, dopant incorporation remains the subject of various investigations.

Ion irradiation is a very attractive tool for several steps in III-nitride based devices' fabrication. The performance of devices such as fast switches [9] and detector [10] has been improved by subjecting them to well-controlled dose of particle irradiation. Compare to the understanding of ion beam process in mature semiconductors (i.e. Si and GaAs), the understanding of the complex ion beam process in III-nitrides is still at its infancy. Much more work is essentially needed to understand the irradiation effect on III-nitride material and device behaviors.

LVMs spectroscopy is a powerful tool in identifying impurities and dopant incorporation in semiconductors. LVMS give rise to sharp peaks in IR absorption spectra. With this method, one can identify the lattice site of the impurity atoms due to the fact that LVMs of impurities are sensitively affected by the atomic structure surrounding the dopant or impurity atom [11]. One typical example is that isotopic composition of the impurity and the surrounding atoms results in well-defined shifts in the vibrational frequencies [12-14].

LVMs of C-H complexes in a series of undoped, Si-doped, and Mg-doped AlGaN samples grown on sapphire substrate by the MOCVD technique have been investigated by using 1MeV proton irradiation. Five distinctive C-H LVM frequencies were observed in the IR spectra recorded before and after proton-irradiating the samples. The evolution of the integrated areas of CH LVMs in proton-irradiated sample is presented as function of irradiation dose.

EXPERIMENTAL DETAILS

All the AlGaN samples used here were grown on sapphire with AlN buffer layer using the MOCVD technique. Al mole fraction ranges from 20% to 60%. Infrared absorbance measurements were performed with a BOMEM FTIR spectrometer, which covers the spectral range of 450-4500 cm⁻¹. A KBr beamsplitter, a globar light source, and a liquid-helium-cooled Si-B detector in conjunction with a continuous flow cryostat were used. A special sample holder was constructed to let the incident light from the spectrometer reach the sample at the Brewster's angle. This configuration proved to be very useful to avoid the interference patterns generated from the substrate as well as from the epitaxial thin film. The spectra were measured at both 300 and 77 K. The samples were irradiated with 1MeV protons and each sample received the following sequential doses 1.0×10^{16} , 5.0×10^{16} and 10.0×10^{16} cm⁻². Infrared absorption measurements were performed before irradiation and after each of the above irradiation doses to investigate the evolution of C-H LVMs spectra and their integrate areas.

EXPERIMENTAL RESULTS

All the samples tested before and after proton irradiation in this study were found to contain five IR peaks in the spectral range of 2846 -2963cm⁻¹. Figure 1 shows an IR spectrum for undoped $\text{Al}_{0.6}\text{Ga}_{0.4}\text{N}$ sample implanted with 1MeV proton and a dose of $1 \times 10^{16}\text{cm}^{-2}$. This spectrum can be resolved into five peaks at 2849, 2870, 2902, 2918 and 2960 cm⁻¹. Based on a comparison between the LVMs measurement in GaN and calculated C-H frequencies in $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$ [15-18], we ascribe these five peaks to symmetric and asymmetric stretching modes of CH_n ($n=1,2,3$) complexes in AlGaN. The absorption peak at 2848 cm⁻¹ is attributed to a stretching mode of CH ; the peaks at 2904 and 2916 cm⁻¹ are attributed to a symmetric and an asymmetric stretching modes of CH_2 , respectively; and the peaks at 2870 and 2960 cm⁻¹ are

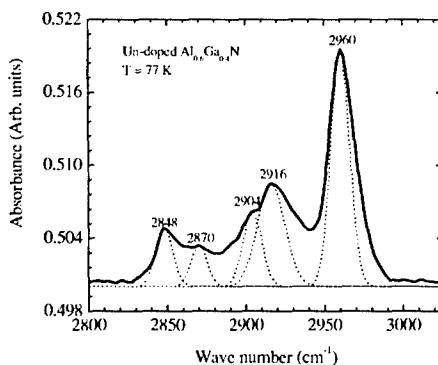


Figure 1. Infrared absorption spectrum measured at 77K for a proton irradiated $\text{Al}_{0.6}\text{Ga}_{0.4}\text{N}$ sample. The IR absorption peaks are resolved into five peaks at 2848, 2870, 2904, 2916 and 2960 cm⁻¹. The solid line is the actual spectrum while the dotted lines are Gaussians added to the spectrum for clarification.

attributed to symmetric and asymmetric stretching modes of CH_3 . Table 1 summarizes the LVMs of C-H complexes in AlGaN, GaN and $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$. From all the spectra of AlGaN samples tested in this study, it was noted that these five peak frequencies are sample dependent.

Table 1. LVMs frequencies of C-H_n in AlGaN, GaN: Mg and $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$. The AlGaN sample was irradiated with 1MeV proton and a dose of $1 \times 10^{16} \text{ cm}^{-2}$. The unit of the frequencies is cm^{-1} .

Stretching Mode	Measured frequencies in AlGaN ^a	Measured frequencies in GaN ^b	Measured frequencies in $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$ ^{c-e}	Calculated frequencies in $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$ ^e
CH	2848 ± 4	2853 ± 1	2860	2850
CH_2 Asymmetric	2916 ± 6	2923 ± 1	2890-2920	2949
CH_2 Symmetric	2904 ± 3	2900 ± 5	2870-2880	2902
CH_3 Asymmetric	2960 ± 3	2956 ± 2	2940-2960	2950
CH_3 Symmetric	2870 ± 3	2870 ± 5	2870-2880	2878

^aPresent work, ^bReference 15, ^cReference 16, ^dReference 17, ^eReference 18.

The LVMs spectra of $\text{Al}_{0.43}\text{Ga}_{0.57}\text{N:Mg}$ tested before and after proton irradiation were shown in Fig. 2. Spectrum (1) was obtained from the as-grown sample. Spectrum (2) and (3) were obtained for this sample after 1MeV proton irradiation over doses of 5×10^{16} and $1 \times 10^{17} \text{ cm}^{-2}$, respectively. This figure shows that proton implantation gives rise to much more significant intensities variation of the CH_3 asymmetric stretching mode than that of other modes. All the other samples tested in this study shows similar behavior. The evolution of the LVMs integrated areas of C-H complexes in undoped, Si-doped and Mg-doped with different doses of proton irradiation is plotted in Fig. 3. Line 1, 2 and 3 are obtained for $\text{Al}_{0.6}\text{Ga}_{0.4}\text{N}$, $\text{Al}_{0.43}\text{Ga}_{0.57}\text{N:Mg}$ and $\text{Al}_{0.56}\text{Ga}_{0.44}\text{N:Si}$, respectively. The LVMs intensities of CH complexes are increased as the irradiation dose is increased in doped samples in the entire irradiation range used in this study and hydrogen atoms seem to continue to form CH complexes in doped samples without reaching the saturation stage. While the LVMs intensities of CH_n in undoped sample were increased first and then start to decrease as the proton irradiation dose is increased above $5 \times 10^{16} \text{ cm}^{-2}$.

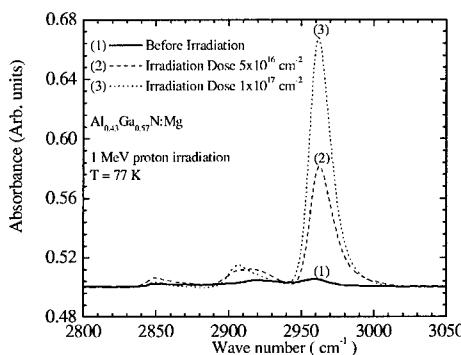


Figure 2. LVMs spectra of C-H_n measured at 77K for a Mg-doped AlGaN sample. Spectrum (1) was obtained for as-grown sample. Spectra (2) and (3) were obtained after proton irradiation with doses of 5×10^{16} and $1 \times 10^{17} \text{ cm}^{-2}$, respectively.

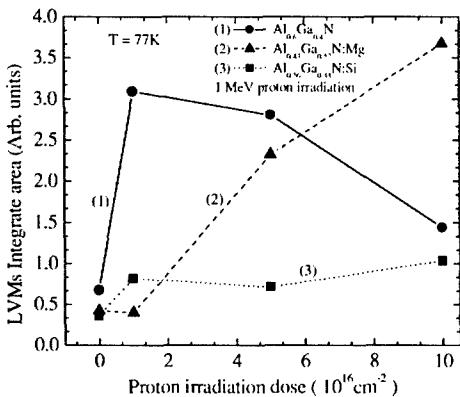


Figure 3. The integrated areas of C-H LVMs in undoped, Si-doped and Mg-doped AlGaN samples plotted as a function of irradiation dose.

DISCUSSIONS

Theoretical studies based on the density functional approach for wurtzite [19-21] and zinc-blende[7, 20] lattices have indicated that the dominant charge state of atomic hydrogen in interstitial solution in GaN is H^+ or H^- depending upon the positions of the Fermi level, with H^0 always being less stable [7, 19-21]. H^+ is the lowest energy state in p-type GaN and H^- is the lowest state in n-type GaN. H^+ and H^0 , on the other hand, are found to be much more mobile than H^- . These studies also indicate that H can form complex by binding with neutral dopants such as acceptor Mg or donor Si on Ga sublattice as well as with residual impurities such as C. Hydrogen can also be in the form of multi-atomic hydrogen related centers (H_2 , $\text{C}-\text{H}_n$, $n=1,2,3$ etc.). Neutral interstitial molecular H_2 has lower formation energy than all three atomic states and was predicted to be energetically preferred for a limited range of Fermi energies near the middle of the bandgap. Energetic ion irradiation can produce gallium (V_{Ga}) and nitrogen (V_{N}) vacancies and interstitial by atomic collisions. The energetic H will initially come to rest at sites with local energy minima. Depending on its mobility, H will either remain at metastable sites or move to lower energy sites at lattice defects or dopants. In the parallel system of AlGaN, we assume that hydrogen states have the same behaviors.

In GaN, C most likely occupies the nitrogen site. The C-H complexes formed when hydrogen passivates substitutional C (C_N) in GaN. Hydrogen was found to be located at a BC site between C and neighboring Ga atoms as is the case for GaAs and InAs [22,23]. Experimental results shows that the CH_n LVMs frequencies in AlGaN are similar to that in GaN. This proves C-H complexes in AlGaN has atomic configuration similar to that in GaN. The slight difference in LVMs frequencies of $\text{C}-\text{H}_n$ in AlGaN and GaN is expected. It is due to the fact that LVMs are highly sensitively to the surrounding atomic structures since Al atoms were added to the crystal, and consequently the atomic structure around C-H complexes in AlGaN is different from that of GaN. Additionally, we observed that LVMs frequencies in AlGaN are sample dependent. This sample dependency could be explained in terms of the presence of dislocations. The strains associated with dislocation are usually sample dependent and can affect the LVMs in a way that their frequencies are sample dependent.

To form $\text{C}-\text{H}_n$ ($n=1-3$), n bonds of C-Ga need to be broken for hydrogen to be incorporated. It is obviously that more energy is needed if more C-Ga bonds are broken.

Therefore, after the proton implantation, the possibility to form C-H is much larger than that of forming C-H₂ and C-H₃, however we observed in all the samples tested in this proton irradiation study that the concentration of C-H₃ is much higher than that of C-H₂ and C-H. This leads to the assertion that hydrogen prefers to form C-H₃ in proton irradiated AlGaN. A possible explanation for this behavior is that there is a substantial number of V_{Ga} in the vicinity of C_N. This is quite possible since the energetic proton bombardment can produce V_{Ga} by atomic collisions, which is a good background to form C-H_n for n > 1 before V_{Ga} is annihilated.

In Fig. 3, we have shown the total integrated areas of C-H complexes LVMs as a function of irradiation dose for the three different samples (undoped, Mg-doped and Si-doped). The LVM results qualitatively provide useful information on the concentration of carbon impurity and the C-H complexes formation rate with proton irradiation dose. For different samples, it is obviously that they have different concentration of carbon impurity. For example, if a sample contains a large concentration of C and by adding H through irradiation, one would expect to observe an increase in the concentration of the C-H complexes. This is demonstrated in Fig. 3. In particular, the data labeled (2) indicates that this sample contains a larger carbon concentration as compared to the other two samples. For undoped and Si-doped samples, the carbon concentration seems to be much lower as judged by the formation of the C-H complexes. The reduction of the total integrated areas in these two samples [data labeled (1) and (3)] might be due to the decomposition of the C-H complexes by proton irradiation. This process is quite feasible in samples where the carbon atoms are completely compensated. Hence, excess proton irradiation will cause partial dissociation of C-H complexes. For the Mg-doped samples, the dominant charge state of H is H⁺ which is a faster diffuser, therefore, part of the H⁺ will form neutral complex with Mg acceptor and part of H⁺ will be attracted by the C_N which is also an acceptor. If a V_{Ga}, which is an acceptor with negative charge state, is near C_N, it may enhances the chances of forming C-H complexes since H⁺ prefer to attach itself to dangling bonds available at the vacancy site. For Si-doped samples, the dominant charge state of H is H⁻ which is less mobile compare to its other two atomic states. The formation of the C-H_n (n=1,2,3) complexes by the diffusion of H⁻ towards substitutional carbon is unlikely in n-type AlGaN since both are ionized acceptors whose negative charges repel one another. The V_{Ga} near C_N will also repel H⁻. For the undoped samples, major part of the energetically H atoms diffuse and combine with carbon to form C-H complexes. From this discussion, it is clear that C-H complexes as judged from the intensity of their LVMs are formed with higher rates in the proton irradiated undoped samples as compared the Mg and Si-doped samples. Figure 3 clearly show that formation rate of

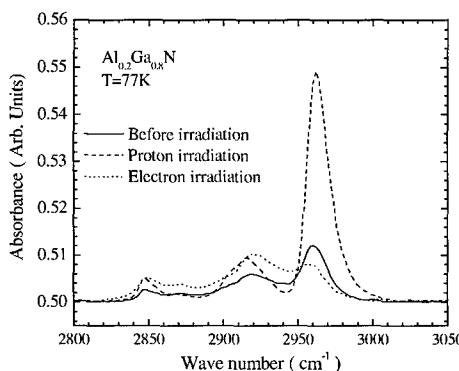


Figure 4. Local vibrational modes spectra measured for two samples cut from the same Al_{0.2}Ga_{0.8}N wafer. The solid line is the spectrum obtained for both samples before irradiation, the dashed line represents the spectrum obtained for the proton irradiated sample (dose=6×10¹⁶ cm⁻²), and the dotted line represent the spectrum obtained for the electron irradiated (dose=1×10¹⁷ cm⁻²) sample.

C-H complexes in the Si-doped sample is much lower than that in updoped and Mg-doped samples.

To illustrate that the observed LVMs are due to C-H complexes, we cut two pieces from an Al_{0.2}Ga_{0.8}N wafer and one piece was irradiated with 1 MeV protons and the other one was irradiated with 1MeV electrons (dose = $1 \times 10^{17} \text{ cm}^{-2}$). The results are shown in Fig. 4. The solid line is the spectrum obtained from the samples before irradiation, the dashed line is the spectrum obtained for the proton-irradiated sample, and the dotted line is the spectrum obtained from the electron irradiated sample. It is clear that proton irradiation increases the formation of C-H complexes as judged by the large increase in the stretching mode frequency of the CH₃ complex. An increase of the stretching mode frequencies for CH₂ and CH is also observed. However, the electron irradiated sample shows a noticeable decrease in the CH₃ stretching mode. This clearly demonstrates that electron irradiation break up the CH₃ complex in good agreement with others [24,25]. There is an increase of the CH₂ and CH concentrations in the electron irradiated sample as seen from the increase in the area under the LVMs stretching modes. This is most likely due to the fact that CH₃ is decomposed into C, H, CH, and CH₂. This behavior is observed in several samples. Additionally, Hall effect measurements show a slight increase in the carrier concentration in the electron irradiation samples. This does not seem to be universal since a few samples show a slight decrease in the carrier concentration after electron irradiation.

CONCLUSION

We presented the local vibrational modes spectra of C-H complexes in proton implanted AlGaN grown by MOCVD technique. Five distinctive C-H LVM frequencies were observed around 2848, 2870, 2904, 2916 and 2960 cm⁻¹, which are slightly different from those observed in GaN. These frequencies are related to stretching symmetrical and asymmetrical vibrational modes of CH_n (n=1,2,3). The evolution of the integrated areas of CH LVMs in proton irradiated samples is presented as function of irradiation dose. In the Mg-doped AlGaN sample, hydrogen atoms (proton) seem to continue to form C-H complexes without reaching the saturation stage in the whole irradiation dose used in this study. This may be due to the fact that carbon is present with a high concentration. Si-doped samples on the other hand show a slight increase in the CH LVM intensities as the dose is increased. While proton irradiation causes a drastic increase in the CH₃ LVM, electron irradiation causes the opposite effect suggesting strongly that the observed LVMs are truly due to CH complexes.

ACKNOWLEDGEMENTS. This work was partially supported by the Air Force Office of Scientific Research Grant No. F49620-00-1-0026. We would like to thank Dr. D. Johnstone for his encouragement and support. We would like to thank D. C. Look and G. C. Farlow of Wright State University for the electron irradiation and J. Chen for the measurements.

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